

Collaborative Research: Polycyclic Aromatic Hydrocarbon Growth Mechanisms in Combustion involving Cyclopentadiene and Indene

NSF Final Project Report

Period of Performance: April 1, 2003 – March 31, 2005

Summary of Project Activities

A two-year project was begun April 1, 2003 to perform experimental and computational studies of polycyclic aromatic hydrocarbon (PAH) growth processes in combustion systems involving cyclopentadiene (CPD). CPD and the compounds with CPD moiety detected in combustion effluents are of interest because of their role as intermediates in the formation of potentially mutagenic PAH which contain five-membered rings, as well as in the formation of fullerenes and soot. CPD and indene readily participate in PAH growth in combustion processes because they form resonance-stabilized radicals which are relatively stable and which are reactive at multiple sites. Study of reactions involving CPD in well-designed molecular systems is needed to better understand the underlying chemistry of PAH growth in combustion and conditions that control the formation of toxic air pollutants and soot.

The experimental and computational studies of this work build on previous work of the by two co-investigators. Previous work by co-PI J. Mulholland at Georgia Tech indicated that cyclopentadienyl (CPDyl) and indenyl radicals add to the non-aromatic p-bonds of the parent molecules (CPD and indene). Subsequent reactions lead to the formation of ortho-fused PAH via one of two pathways. One involves expansion of both five-membered rings to form PAH with only six-membered rings by a route modified from that proposed for CPDyl radical combination to form naphthalene. The other involves formation of a norbornenyl-type bridged intermediate followed by ring opening and loss of a C_1 species to form PAH that retain one CPD moiety. This second pathway represents a route of PAH formation not previously studied. Experimental studies at Georgia Tech have extended the previous work in two areas: PAH formation from CPD, acenaphthylene, styrene, and phenanthrene, and polychlorinated naphthalene (PCN) formation from mono- and di-chlorophenols via CPDyl intermediates.

At the University of Utah, co-PI A. Violi has applied quantum mechanical theory to the study of carbon growth processes involving acenaphthylene. In this work, *ab initio* modeling of the CPD/indene system was used to refine computational methods and then to study new CPDyl addition pathway identified in the experimental studies. Modeling work has focused on identification of reaction pathways of PAH growth in combustion conditions. Compounds that contain the CPD moiety are of interest because of their role as intermediates in the formation of potentially mutagenic PAH which contain five-membered rings, as well as in the formation of fullerenes and soot. As computational tool, a methodology for accelerating molecular dynamics calculations has been used for purposes of screening and evaluating alternative reaction pathways.

Results of this research improve the understanding of chemical mechanisms of PAH and soot formation in combustion systems. The approach combined experimental and computational expertise of co-investigators and doctoral and masters students at two institutions.

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Findings

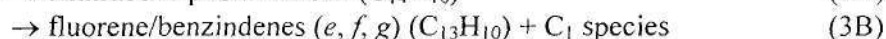
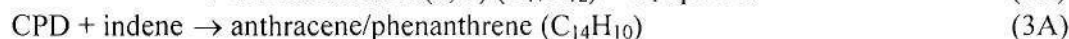
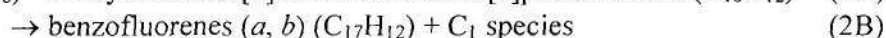
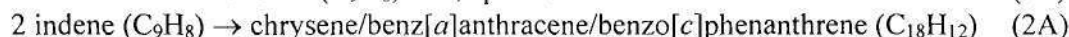
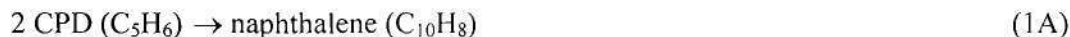
The experimental and computational studies of this work build on previous work of the by two co-investigators. Previous work by PI J. Mulholland at Georgia Tech indicated that cyclopentadienyl (CPDyl) and indenyl radicals add to the non-aromatic π -bonds of the parent molecules (cyclopentadiene and indene). At the University of Utah, PI A. Violi has applied quantum mechanical theory to the study of carbon growth processes involving acenaphthylene, which contains the cyclopentadiene moiety.

1. Experimental Studies (Georgia Tech)

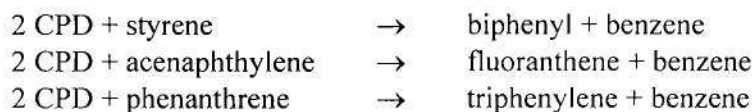
Experimental studies at Georgia Tech have extended the previous work in two areas: polycyclic aromatic hydrocarbon (PAH) formation from cyclopentadiene (CPD), acenaphthylene, styrene and phenanthrene, and polychlorinated naphthalene (PCN) formation from chlorinated phenols via CPDyl intermediates. Findings are highlighted below.

1.1 PAH Growth from Pyrolysis of CPD, Acenaphthylene, Styrene, and Phenanthrene

The formation of five-membered rings in combustion is of particular interest due to the high reactivity and toxicity of many compounds that contain these moieties. PAH with peripherally fused five-membered rings demonstrate a greater facility to undergo certain kinds of reactions, such as isomerization involving intramolecular rearrangement. Recent research in our laboratory addresses PAH growth from indene and CPD. PAH products from dicyclopentadiene (DCPD) and indene pyrolysis at 550-850°C, temperatures below which ring fragmentation pathways are dominant, were more numerous than expected. Observed PAH products are given below in equations by 1 through 3. Reaction pathways were proposed to explain the formation of two sets of products from each combination of CPD and indene. Equations 1A, 2A and 3A show products that can be formed either by a radical-radical mechanism or by radical-molecule pathways. Equations 1B, 2B and 3B show products formed by radical-molecule pathways in which a norbornenyl-type (bridged) radical intermediate is formed. The products (indene, benzofluorenes, fluorene and benzindenes) retain one CPD moiety. The C_1 species that is produced from intramolecular addition pathway combines with CPD or indene to form benzene or naphthalene, respectively.



The objective of this research was to investigate PAH formation and growth from CPD and CPDyl radical with aromatic species containing different types of π bonds; namely, styrene, acenaphthylene and phenanthrene. Styrene is a simple aromatic molecule that contains a vinyl substituent that is most susceptible to radical addition. Acenaphthylene is a fully conjugated PAH containing an external five-membered ring. Phenanthrene has a reactive π bond that is part of a six-membered ring. In all three cases, rearrangement of the addition product to form a structure containing a dihydrofulvalene moiety, which is a prerequisite for PAH fusion by the CPD-to-naphthalene mechanism is not possible without disrupting an aromatic ring. Therefore, the hypothesis tested in the proposed study is that the major PAH products from CPD reactions with the three test compounds would be those listed below, produced via norbornenyl-type bridged intermediates.



PAH formation and growth from pyrolysis of CPD and the mixtures of CPD, acenaphthylene, styrene and phenanthrene was studied in a laminar flow, isothermal quartz tube reactor with 1.7 cm internal diameter and 40 cm length over a temperature range of 600°C to 1000°C. Dicyclopentadiene (DCPD), acenaphthylene, styrene and phenanthrene are commercially available. DCPD is converted to CPD when heated above its boiling point (170°C). DCPD was heated to liquid form (34°C) and fed by a syringe pump into a heated glass vessel (200°C) where the reactant was vaporized and in a nitrogen gas stream. The molar ratio of CPD to acenaphthylene in the gas entering the reactor was 4 to 1. The CPD to styrene molar ratio was 1 to 1. The CPD to phenanthrene molar ratio was 8 to 1. The total reactant concentration was nominally 0.8%. A nominal reactor residence time of 2-3 seconds was maintained.

The product stream was immediately quenched at the outlet of the reactor and collected in a dual ice-cooled dichloromethane trap. Soot, defined as the dichloromethane insoluble fraction, was separated by vacuum filtration and measured gravimetrically. The entire gas stream was immediately quenched at the outlet of the reactor.

Filtered samples were analyzed using by a Hewlett-Packard 6890 series gas chromatography with HP-5MS column (30m, 0.25 mm i.d., 0.25 μ m film thickness) coupled to a Hewlett-Packard 5973 mass spectrometer. Due to high volatility of CPD and its co-elution with the solvent, CPD concentrations were separately measured from gas samples with direct injection of the gas samples into the GC-MS column. Aromatic products were identified and quantified using chemical standards, which included benzene, indene, naphthalene, toluene, styrene, fluorene, phenanthrene, anthracene, 2-methyl indene, and 1,2-dihydrofulvalene.

1.1.1 Formation of Naphthalene, Indene, and Benzene from CPD pyrolysis

CPD yields from DCPD reactant, which were not measured in the previous studies [1-2], were greater than 90% of carbon input until 700°C, indicating high conversion of DCPD to CPD and good reactant recovery. DCPD was below detection. Above 700°C, CPD begins to react in significant amounts with more than 99% of the CPD reacted at 825°C. Soot formation was observed at 850°C and above, with soot yield increasing with temperature. As expected, the major products from CPD pyrolysis were benzene, indene and naphthalene. The amount of

indene produced exceeded that of naphthalene and benzene for temperatures lower than 775°C. Between 775°C and 900°C, naphthalene yield was greatest, and above 900°C, benzene formation becomes predominant.

Based on previous experimental work on indene [1] and a mixture of CPD and indene [2], and on the computational study of CPD [3], possible reaction pathways from CPD are proposed to explain the major products of CPD pyrolysis (Figure 1). Indene and benzene were formed through the intramolecular addition routes (R1 and R2) whereas naphthalene was formed via β -scission routes (R3, R4 and R5). Identification of stable intermediates, written in bold in Figure 1, supports the proposed formation routes. The intramolecular addition products were favored at low temperatures whereas β -scission product was favored at high temperatures.

In addition to the published pathways (R1-R4), C-C β -scission was proposed as a new reaction channel for naphthalene formation from CPD, shown as R5 in Figure 1. Ring expansion of cyclopentadiene to a six-member ring via the formation of a three-member ring, analogous to the conversion of methylcyclopentadienyl radical to benzene [4-5], leads to the formation of butyl-cyclohexadienyl radical. Cyclodehydrogenation leads to naphthalene. The experimental identification of dihydro-naphthalene, which is not expected from the C-H β -scission routes, supports the proposed C-C β -scission route.

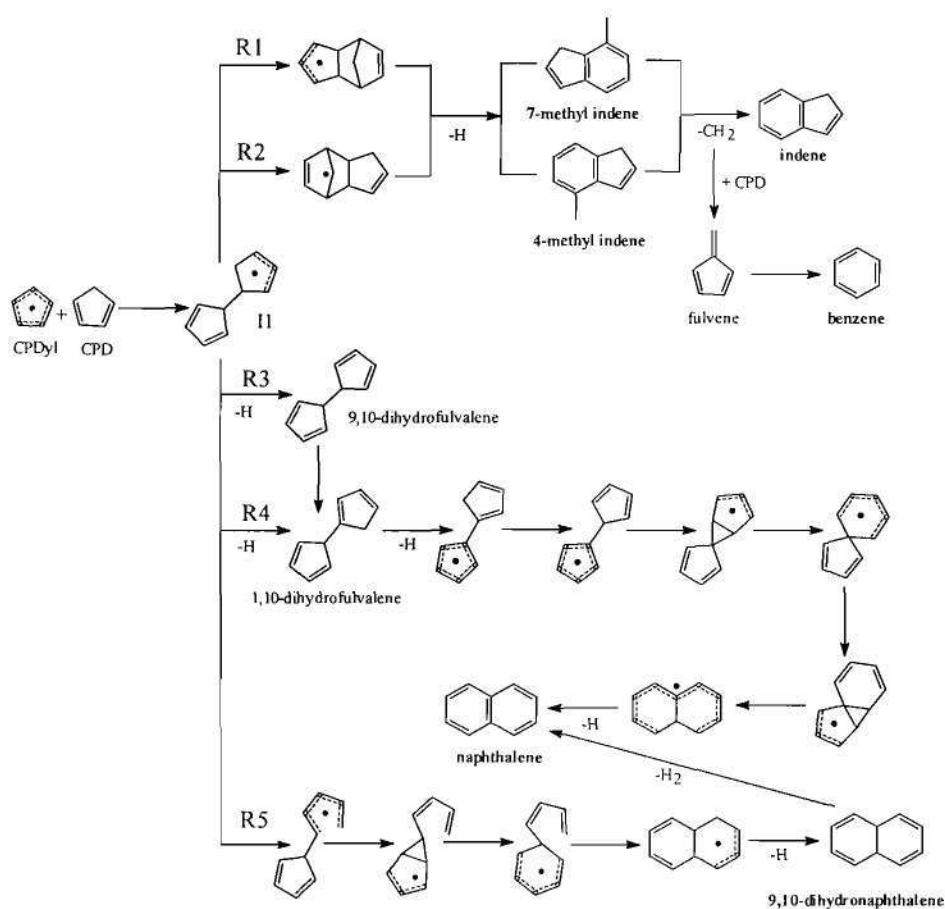


Figure 1. Reaction pathways to indene, benzene and naphthalene from CPDyl-CPD (II). Products observed in experiments are written in bold.

1.1.2 CPD-Acenaphthylene Mixture Pyrolysis

Major products from the mixture of CPD and acenaphthylene pyrolysis were naphthalene, indene and benzene. High yields of benzene, indene and naphthalene suggest the CPD-CPD reaction is a dominant reaction in the pyrolysis of CPD-acenaphthylene mixture. Other aromatic compounds produced are toluene, styrene, fluorene, phenanthrene, and anthracene. Formation of toluene and styrene can be explained by the reaction involving CPD, benzene and acyclic fragments. Fluorene, phenanthrene and anthracene are likely to be formed from the CPD-indene reaction. Formation of C-16 and C-17 species that are expected to be formed from the reaction of CPD and acenaphthylene were not observed at temperatures below 800°C. Observed C-16 compounds were fluoranthene and acephenanthrylene.

Acenaphthylene is both a reactant and a product in the pyrolysis of CPD-acenaphthylene mixture because formation of acenaphthylene was observed even from the pyrolysis of CPD alone. In order to have a better assessment on PAH growth from the reaction of CPD and acenaphthylene, yields of aromatic products from the pyrolysis of CPD-acenaphthylene mixture are compared with those from the pyrolysis of CPD alone. Molar ratios of naphthalene, indene and benzene to CPD input from both pyrolysis of CPD-acenaphthylene mixture and CPD alone are almost same over the temperatures studied; the results support that the CPD-CPD reaction is the dominant reaction in the pyrolysis of CPD-acenaphthylene mixture. The biggest difference between CPD and CPD-acenaphthylene mixture pyrolysis is yields of fluoranthene and acephenanthrylene (Figure 2). Both fluoranthene and acephenanthrylene are likely formed from the reaction of CPD and acenaphthylene. The yield of fluoranthene from CPD-acenaphthylene mixture is greater by a factor of 4 than that from CPD alone. In addition, the ratio of yield of acephenanthrylene from CPD-acenaphthylene mixture relative to that from CPD alone is 3 to 1.

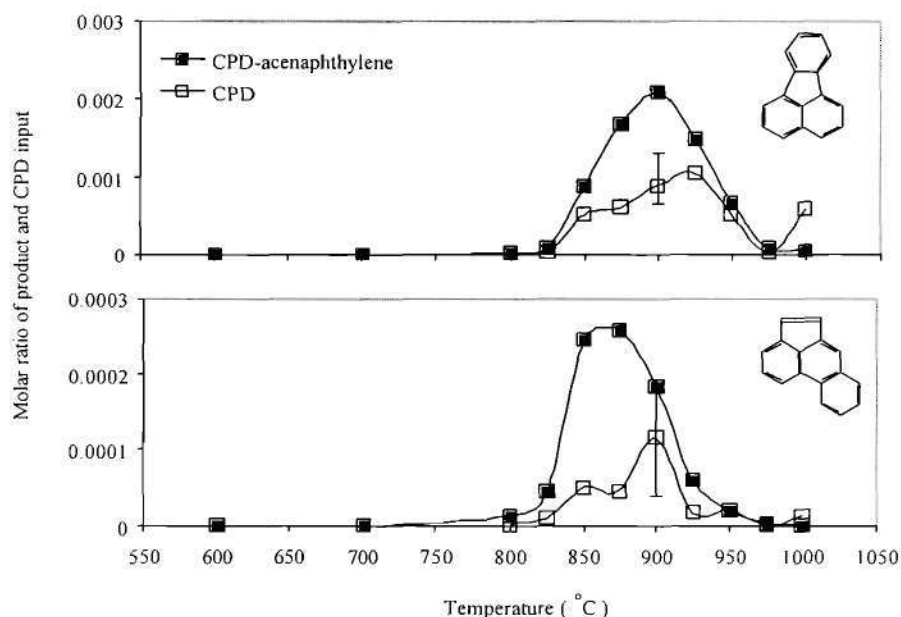


Figure 2. Comparison of the C₁₆H₁₂ products from CPD and acenaphthylene-CPD mixture pyrolysis; fluoranthene (top) and acephenanthrylene (bottom). Filled symbols are used for CPD-acenaphthylene mixture pyrolysis products and hollow symbols are used for CPD pyrolysis products.

In the case of the CPD-acenaphthylene reaction, rearrangement of the addition product to form a structure containing a dihydrofulvalene moiety, which is a prerequisite for PAH fusion by the CPD-to-naphthalene mechanism, is not possible without disrupting an aromatic ring. None of the $C_{17}H_{14}$ products were detected over the entire temperature studied, suggesting that the contribution of the pathway via three-member ring closures and openings was not important. Thus, it is concluded that the PAH products from CPD reaction with acenaphthylene were produced via norbornenyl-type bridged intermediates. Here, the reaction pathways for $C_{16}H_{12}$ products from the mixture of CPD and acenaphthylene are proposed (Figure 3). Trace amounts of intermediates with molecular formula $C_{17}H_{12}$ in the formation of these products were also detected, but those intermediates were not identified due to the lack of standards.

Among four channels, the pathway of CPDyl radical addition to the external π -bond in acenaphthylene appears to be favored because the yield of fluoranthene was an order of magnitude higher than the yield of acephenanthrylene (Figure 2) and only trace amount of aceanthrylene (not shown) was observed. On the other hand, addition of acenaphthylenyl radical to a π -bond of CPD molecule would also lead to the same $C_{16}H_{12}$ products observed. That is, however, much less favorable channel since radical formation from fully conjugated PAH is not as easy as that from CPD. Any products from the aryl-aryl reaction of acenaphthylene were not observed. Although the yields of the products from CPD-acenaphthylene reaction is relatively low, the increased soot formation compared to CPD pyrolysis was observed at the temperatures studied, indicating carbon growth. Low product yields and less variety of products compared to the pyrolysis of CPD alone suggest that the carbon growth products from addition of carbon fragments (e.g. methyl) are also small.

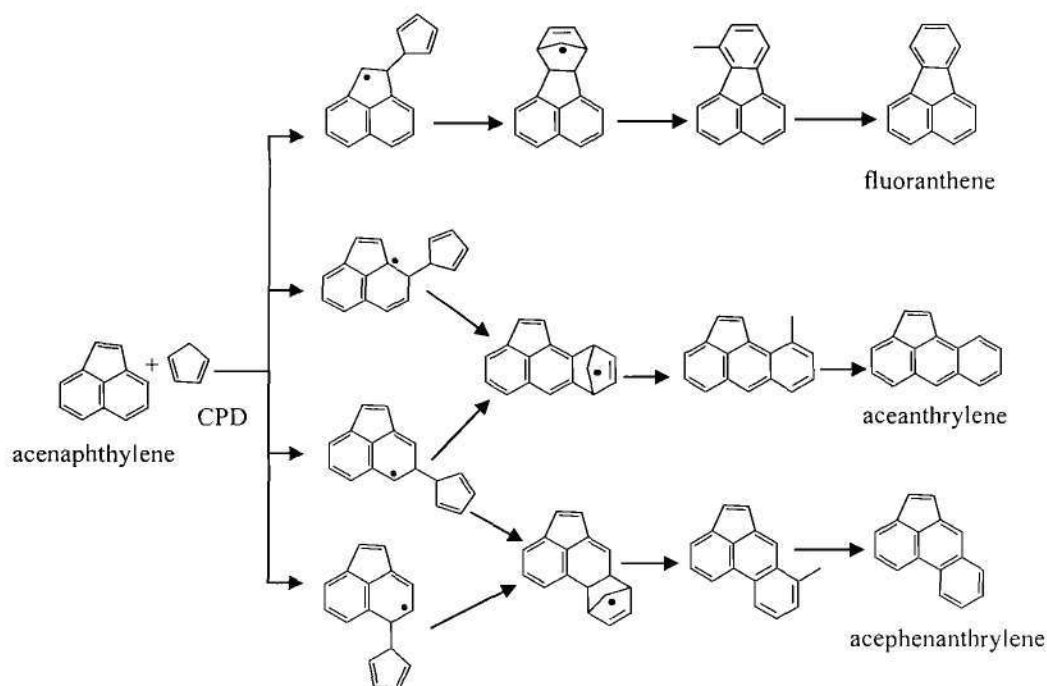


Figure 3. Hypothesized pathways of aromatic growth from CPD-acenaphthylene reaction.

1.1.2 CPD-Styrene Mixture Pyrolysis

Major products were benzene, toluene, naphthalene and indene. Yields of benzene and naphthalene increased with temperature and leveled off. Unlike CPD and CPD-acenaphthylene mixture pyrolysis, benzene and toluene yields were greater than indene and naphthalene yields at low temperatures, indicating that benzene and toluene are likely formed from the decomposition of styrene. High yields of indene and naphthalene suggest that the reactivity of CPD to itself is much higher than to styrene.

Formation of biphenyl, fluorene and phenanthrene was observed at temperatures of 700°C and above. Both fluorene and phenanthrene can be formed from the reaction between CPD and indene based the previous results from CPD-indene mixture pyrolysis [1-2]. Formation of indene, naphthalene, fluorene and phenanthrene suggests the existence of both a radical-radical pathway analogous to the CPD-to-naphthalene mechanism and a radical-molecule pathway involving a bridged intermediate in CPD-styrene mixture pyrolysis.

To more easily compare PAH formation and growth from the reaction of CPD and styrene with those from the reaction of CPD alone, the product yields are expressed in the molar ratio of product yield and CPD input (Figure 4). The yield of benzene from CPD-styrene mixture is greater than that from CPD with a factor of 2. Also, the ratio of biphenyl yield to CPD input from CPD-styrene mixture is a couple of order greater than that from CPD alone. These results are consistent with our hypothesis.

PAH formation pathways from the mixture of CPD and styrene are depicted in Figure 5. A radical-radical pathway of CPDyl radicals produces naphthalene whereas a radical-molecule pathway of CPD leads to indene and benzene. Indene from both CPD-CPD and CPD-styrene reactions can further react with CPD to produce fluorene via the pathway involving a bridged intermediate and phenanthrene and anthracene via the pathway involving three-member ring closures and openings. In case of benzene formation from CPD-styrene mixture, a dominant route might, however, be the decomposition of styrene. Also, CPD-CPD reaction might be a dominant reaction channel for indene formation.

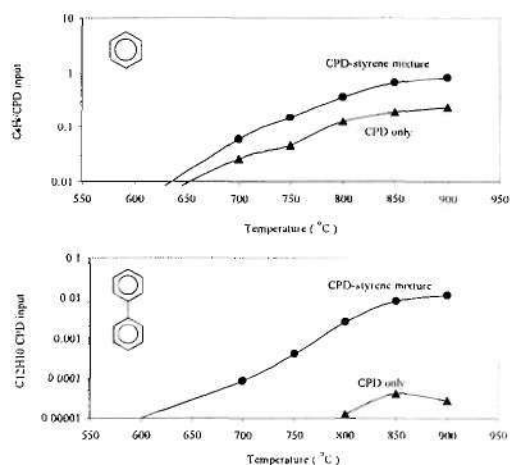


Figure 4. Products from CPD-styrene mixture and CPD pyrolysis; benzene (top) and biphenyl (bottom).

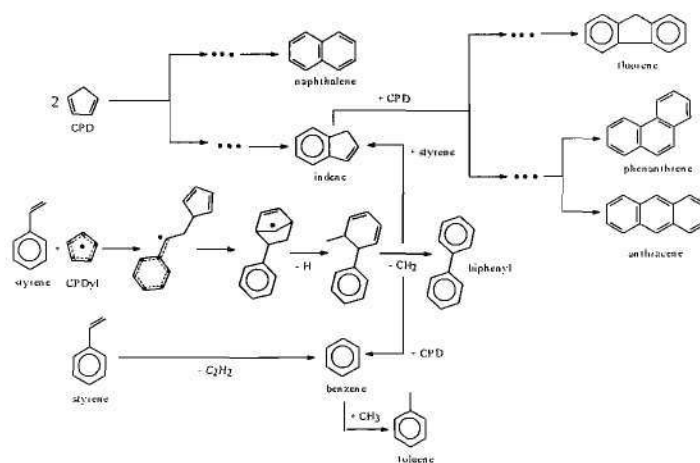


Figure 5. PAH growth pathways from CPD-styrene mixture pyrolysis.

1.1.3 CPD-Phenanthrene Mixture Pyrolysis

Benzene, naphthalene and indene were the major products from CPD-phenanthrene mixture pyrolysis. Also, toluene, anthracene, fluorene and acenaphthylene were observed. Lack of high molecular weight products and high recovery rate of phenanthrene indicates that phenanthrene is much less reactive than CPD. Given the high yields of naphthalene, indene and benzene, the major reaction channel appears to be the reaction of CPD to itself, consistent with the results from CPD-styrene and CPD-acenaphthylene mixture pyrolysis.

Contrary to the hypothesis, formation of triphenylene was not observed. Our rationale is that the reactivity of CPDyl radical to phenanthrene is much less than that to CPD itself and/or amount of phenanthrene in CPD-phenanthrene mixture may not be adequate to yield observable quantity of products from CPD-phenanthrene reaction.

1.2 Polychlorinated Naphthalene Formation from Chlorinated Phenols via CPDyl intermediates

To test the first hypothesis that polychlorinated naphthalenes (PCNs) can be formed from chlorinated phenols via cyclopentadienyl radicals in post-combustion gas, the slow combustion of three chlorophenols (CPs) was studied in a flow reactor. Contrary to the *a priori* hypothesis, different distributions of PCN isomers were produced from each CP. To explain these distributions and the observed correlation between polychlorinated dibenzofuran (PCDF) and PCN yields, a mechanism was proposed that builds on published mechanisms of PCDF formation from chlorinated phenols and naphthalene formation from dihydrofulvalene to account for differences between the *a priori* hypotheses and the experimental results. In addition, the effect of temperature on gas-phase PCN and PCDF formation from CPs was also investigated to gain further mechanistic insight on these processes. The proposed mechanism was also tested for PCN and PCDF formation from six dichlorophenols (DCPs) at 600°C.

A laminar flow, isothermal quartz tube reactor (40 cm in length and 1.7 cm in diameter) was used to study PCN formation from three CPs and six DCPs. Two of the chlorophenols, 2-CP and 3-CP, were heated to liquid form and fed by syringe pump into a heated glass vessel where the reactant was vaporized and mixed with a nitrogen/oxygen gas stream. The third chlorophenol, 4-CP, formed a melt that was too viscous to be fed by syringe. This reactant was heated directly in the glass vessel and vaporized at the same rate as the syringe-fed liquid reactants were fed. The gas stream entering the reactor consisted of nitrogen with 8% oxygen and 0.3% CP vapor. Experiments were conducted in triplicate at 600°C, the temperature at which total PCN yield was greatest; duplicate experiments for 2-CP were conducted at 700, 725 and 750°C.

DCP reactant was dissolved in benzene (1:2 molar ratio) to get the DCP reactant into solution. Experiments were conducted at 600°C, the temperature at which PCN yields were greatest under our experimental condition [6]. Nitrogen with 8% oxygen and 0.1% DCP vapor was injected into the reactor. Experiments with benzene only (i.e. without DCP reactant) demonstrated that phenol was almost entirely derived from hydroxylation of benzene and not dechlorination of DCP. Otherwise, benzene was not reactive under these conditions.

Identification and quantification of PCN, PCDD, and PCDF congeners was accomplished with a Hewlett-Packard 6890 series gas chromatography with HP-5MS column (30m, 0.25 mm i.d., 0.25 μ m film thickness) coupled to a Hewlett-Packard 5973 mass spectrometer. For quantification, the mass spectrometer was operated in selective ion mode at the two most

intensive and characteristic ion masses. PCN isomers were identified based on the elution time and order of PCNs in Halowax 1001, 1014, and 1051 standards [7-8]. Universal response factors were used for PCN and PCDD/Fs based on naphthalene (N), dibenzo-p-dioxin (DD) and dibenzofuran (DF), respectively. In addition, CO measurements in the exhaust gas were performed with a Hewlett-Packard 5890 II series gas chromatography coupled to thermal conductivity detector (TCD) with HP-MOLSIV column (15m, 0.53 mm i.d., 0.25 μ m film thickness).

1.2.1 Chlorinated Naphthalene Formation from Chlorophenols

Based on the observed simultaneous formation of PCNs and PCDFs from CPs, PCN formation pathways from CPs are proposed that build on the dihydrofulvalene-to-naphthalene mechanism [3]. The proposed overall reaction pathway for PCDF and PCN formation from chlorophenols is depicted in Figure 6. Chlorophenols can lose hydrogen or chlorine to produce chlorophenoxy or phenoxy (with hydrogen migration) radicals. These resonance-stabilized radicals can couple at unchlorinated ortho carbon sites to produce the diketo-tautomer of DOHB (step 1 in Figure 6). In PCDF formation, this intermediate undergoes keto-enol tautomerization to form DOHB (step 2); subsequent elimination of H₂O yields the PCDF product (step 3). Alternatively, dihydrofulvalene is formed by CO elimination from the diketo-dimer intermediate (step 4). Elimination of CO from both stable and radical systems of phenol has been studied [9-11]. Subsequent fusion of dihydrofulvalene to form naphthalene products is depicted by step 5. Unlike PCDF formation, PCN formation from the diketo-dimer intermediate may involve chlorine loss. Experimental results indicate that the 9,10 carbon atoms of 9,10-dihydrofulvalene are likely to be translated to the 9,10 carbon atoms of naphthalene.

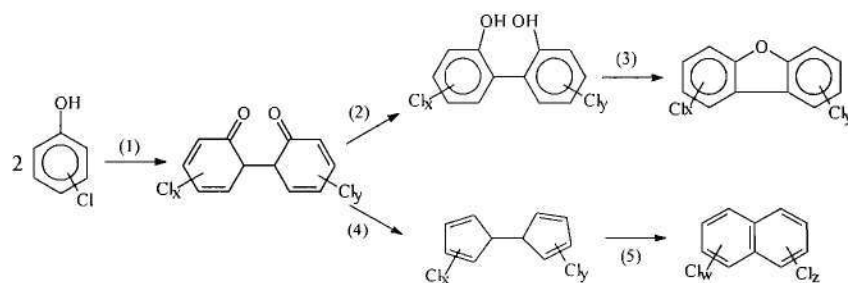


Figure 6. Overall PCDF and PCN formation pathways from chlorophenols.

As temperature increased, the ratio of naphthalene to dibenzofuran products increased for each of the CP reactants. The ratio was greatest for 2-CP and least for 3-CP over the temperature studied (Figure 7). These results suggest that CO elimination (step 4 in Figure 6) that leads to naphthalene formation becomes increasingly favored relative to tautomerization (step 2 in Figure 6) that leads to dibenzofuran formation as temperature increases.

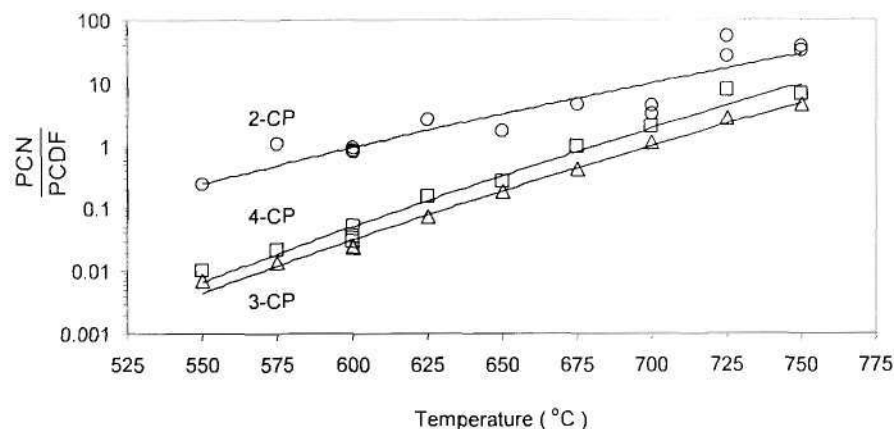


Figure 7. Ratio of total naphthalene to total dibenzofuran product yields from CPs.

PCDF isomer distributions from CPs over temperature show that the MCDF and DCDF isomer distributions are only weak functions of temperature; however, the MCN and DCN isomer distributions from 2-CP and 4-CP are strong functions of temperature, whereas the MCN and DCN isomer distributions from 3-CP are not (Figure 8). The selectivity to particular PCN isomers decreased as temperature increased; that is, the ratios tended to go toward one.

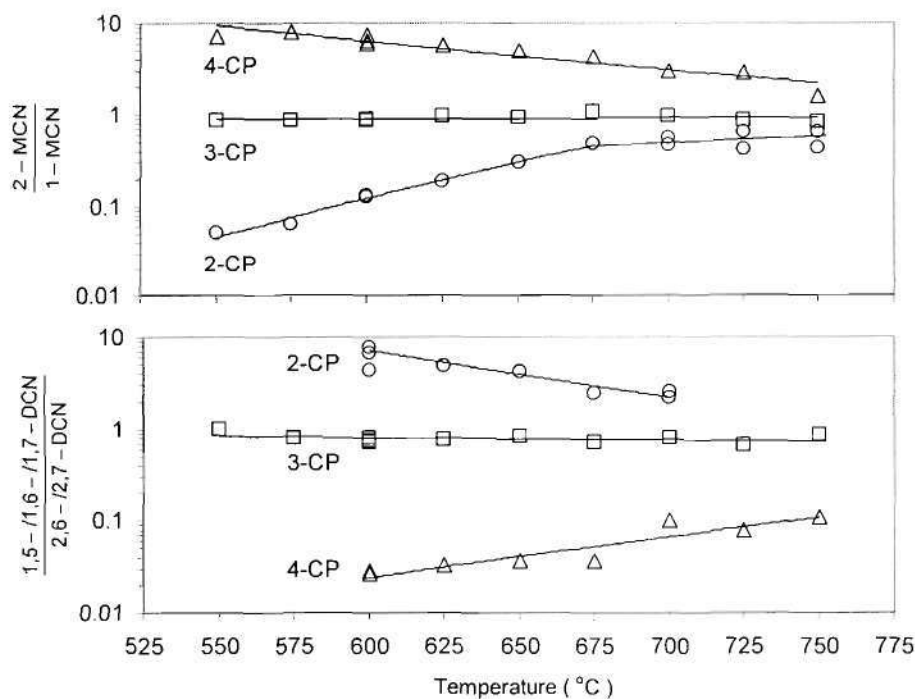


Figure 8. Ratios of MCN and DCN isomers from chlorophenols.

1.2.2 Polychlorinated Naphthalene Formation from Dichlorophenols

The PCN and PCDF congener patterns observed from dichlorophenols (DCPs) are consistent with the prediction based on the proposed PCN pathways involving CPDyl intermediate. From DCP experiments, T_4 CNs were detected only in trace amounts, and only from 3,4-DCP. This suggests that the major route of PCN formation from chlorinated phenols is by loss of at least one chlorine atom. The total T_4 CDF yields, on the other hand, were similar in magnitude to the yields of other homologues. In particular, the two DCPs without ortho chlorine (i.e. 3,5- and 3,4-DCPs) had high T_4 CDF yields. Yields of N, MCNs and DCNs were of similar order of magnitude. The PCN homologue with greatest yield was unchlorinated naphthalene from 2,3-, 2,4- and 2,5-DCPs, MCN from 3,5- and 2,6-DCPs, and DCN from 3,4-DCP. 3,4-DCP produced the greatest T_3 CN yield.

Regarding PCDF formation, 3,4- and 3,5-DCPs produced more T_4 CDF products than other homologues. For each of the six DCPs, DCDF product yield exceeded T_3 CDF product yield, and DF product yield exceeded MCDF product yield. These results are consistent the major PCDF precursors being DCP reactant and phenol from hydroxylation of benzene. PCDFs are formed without loss of chlorine; therefore, two DCPs produce T_4 CDFs, DCP and phenol produce DCDFs, and two phenols produce DF. MCDF and T_3 CDF products are formed from DCP and MCP formed by DCP dechlorination. MCP yields were significantly lower than phenol yields.

Identification of chlorinated dibenzofuran, dibenzo-p-dioxin and naphthalene congeners from slow combustion of each of the six DCPs supports a proposed mechanism of PCN formation that involves the same phenoxy couple intermediate as that for PCDF formation. This link between PCN and PCDF formation may explain observed correlations of PCN and PCDF yields in combustion systems. These results also provide data that can be used to computationally study congener-specific mechanisms of PCN formation from chlorinated phenols. PCN formation from phenols with 2,6 chlorine substituents requires further study.

1.3 Preliminary Modeling of CPD Reactions

Preliminary modeling of the CPD reaction schemes depicted in Figure 1 were performed using the semiempirical PM3 method. Results shown in Figure 9 suggest that the PM3 method might be used as a screening tool for higher level molecular study. Figure 10 indicates that the pathways via the norbornenyl structures have the lowest energy barriers. This result is consistent with indene being the major product from CPD pyrolysis at low temperatures. The more detailed computational study presented next provides more quantitative results.

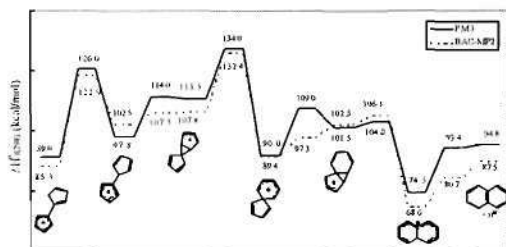


Figure 9. Comparison of PM3 and BAC-MP2 Methods for CPD-CPDyl to naphthalene.

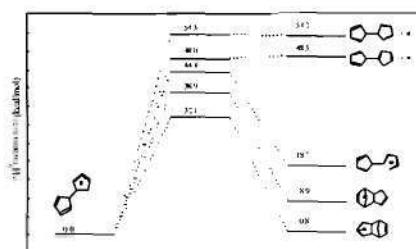


Figure 10. Comparison of energies of CPD-CPDyl unimolecular reaction channels.

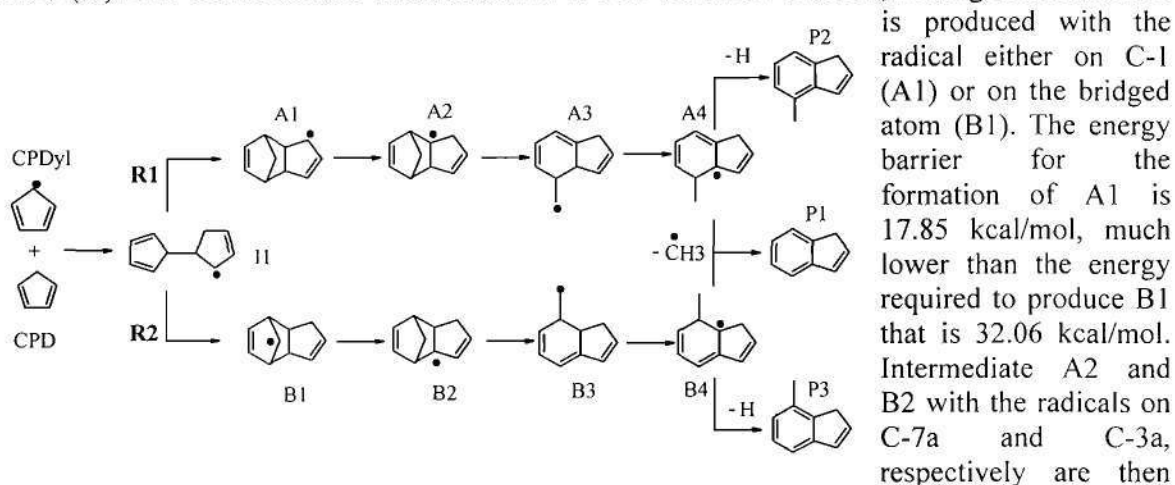
2. Computational Studies (University of Utah)

Modeling studies at the University of Utah have focused on two main areas: analysis of the reaction pathways for polycyclic aromatic hydrocarbon (PAH) formation from cyclopentadiene (CPD) pyrolysis and cyclodehydrogenation reactions to cyclopenta-fused PAH. Findings are highlighted below.

2.1 Formation of Naphthalene, Indene and Benzene from Cyclopentadiene Pyrolysis

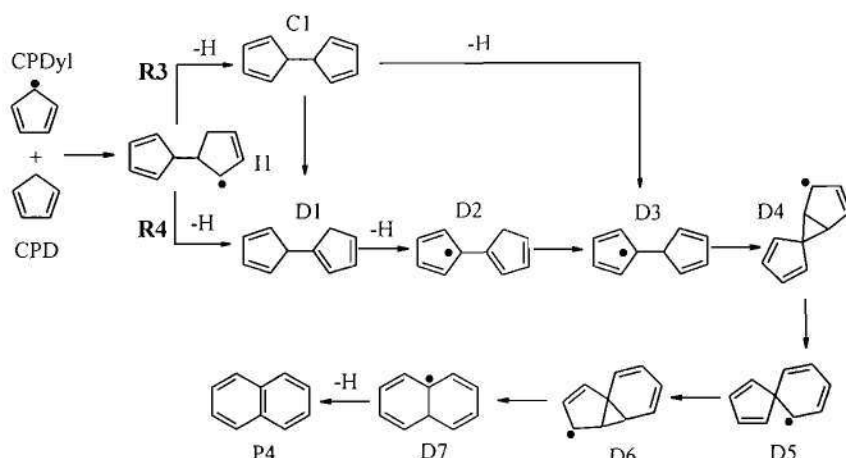
Polycyclic aromatic hydrocarbon growth from cyclopentadiene pyrolysis has been investigated using the B3LYP/6-31G(d,p) level of theory. The experimental data obtained in a laminar flow reactor, which have been presented in section 1.1.1 have been used to guide and validate the computational results.

The figure below shows the reaction pathways for the addition of CPD to CPDyl to produce indene (pathways R1 and R2). The reaction of CPD with CPDyl begins with the addition of the cyclopentadienyl radical to the π -bond of CPD to produce a resonantly stabilized CPD-CPDyl dimer (I1). The intermolecular addition barrier is 11.5 kcal/mol. From I1, a bridged intermediate



is produced with the radical either on C-1 (A1) or on the bridged atom (B1). The energy barrier for the formation of A1 is 17.85 kcal/mol, much lower than the energy required to produce B1 that is 32.06 kcal/mol. Intermediate A2 and B2 with the radicals on C-7a and C-3a, respectively are then obtained through hydrogen migration reactions. The subsequent bridge opening step produces bicyclic intermediates with the radical on the methyl group (A3 and B3). The energy barriers for the formation of A3 (37.9 kcal/mol) and B3 (38.2 kcal/mol) are similar. A3 and B3 undergo further 1,3-H shift to produce A4 (the radical is on C-3a) and B4 (the radical is on C-7a). The loss of the methyl group produces indene (P1). The energy barriers for $A4 \rightarrow P1 + CH_3$ and $B4 \rightarrow P1 + CH_3$ are 22 and 19.7 kcal/mol, respectively.

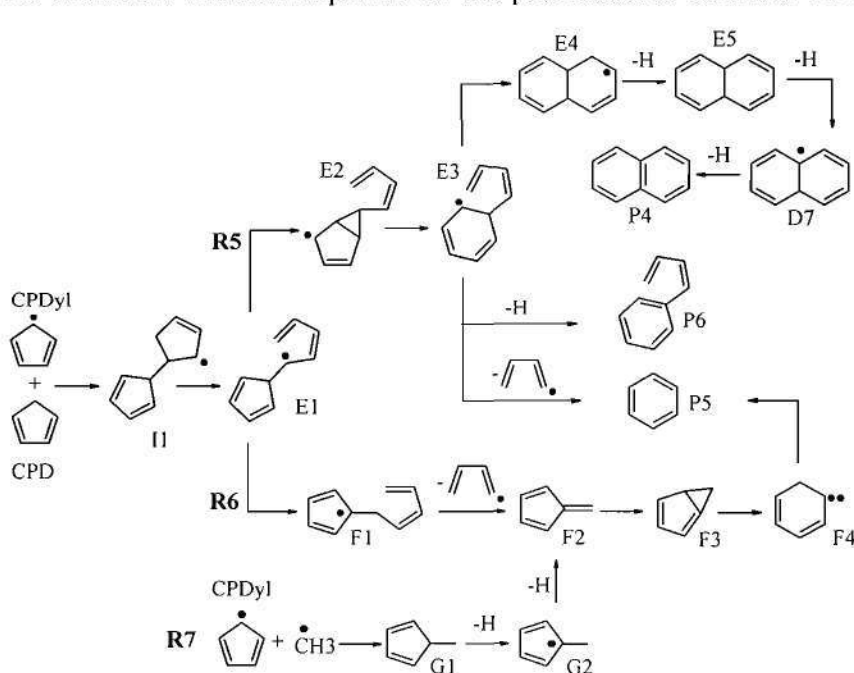
As an alternative, A4 can undergo H elimination to form 4-methyl indene (P2) and in a similar way B4 produces 7-methyl indene (P3). The figure below shows the C-H bond β -scission pathways R3 and R4 that lead to the formation of naphthalene. The reaction mechanism of combining two CPDyl radicals to form naphthalene has been already investigated by Melius et al.³ using the Bond Additivity-Corrected fourth-order perturbation Møller-Plesset (BAC-MP4) and BAC-MP2 levels of theory. Through H elimination, I1 forms 9,10-dihydrofulvalene (C1), which rearranges to form the more stable 1,10-dihydrofulvalene (D1).



The energy barriers for $I1 \rightarrow C1 + H$ and $C1 \rightarrow D1$ are 48.45 and 24.06 kcal/mol, respectively. The loss of H-atom from the 10-carbon site of D1 produces a resonance-stabilized radical D2 and its isomerization by 1,3-H shift leads to D3, which can also be formed by eliminating a H atom directly from C1. D3 undergoes three-

membered ring closure (D4) and subsequent opening to complete the ring expansion (D5). At the B3LYP/6-31G(d,p) level, the activation energy for the reaction $D3 \rightarrow D4$ is 12.4 kcal/mol while the reaction $D4 \rightarrow D5$ has an energy barrier of 23.2 kcal/mol. This process can be repeated, converting a second five-membered ring to six-membered ring. A final C-H bond β -scission yields naphthalene and H atom.

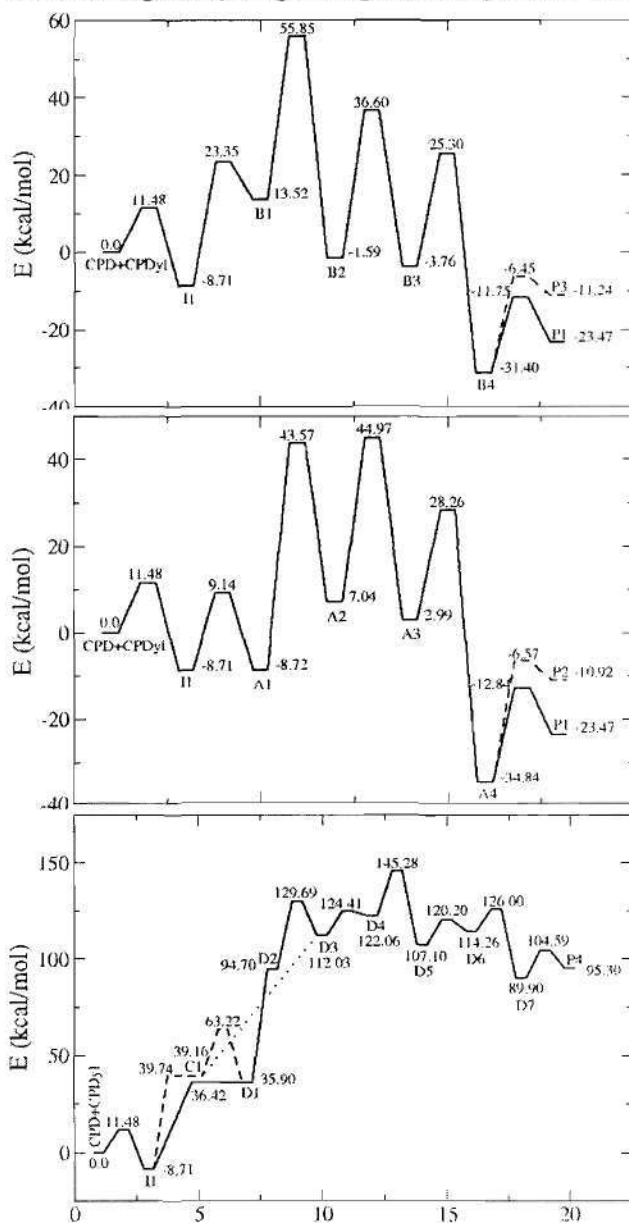
Competing with the above mentioned pathways, new reaction pathways are proposed that involve the β -scission of a C-C bond. The figure below reports the various steps for pathways R5 and R6. Pathway R5 leads to the formation of either naphthalene or benzene, while pathway R6 shows the reaction sequence for the production of benzene. The molecule-radical dimer I1



undergoes a β -scission of the C-C bond, opening one of the two five-membered rings, to form intermediate E1. The energy barrier required for this step is 41.21 kcal/mol. The other five-membered ring expands to six-membered ring via a three-membered ring closure step to form E2 first and then E3. The barriers for the reactions $E1 \rightarrow E2$ and $E2 \rightarrow E3$ are 15.3 and 19.6 kcal/mol, respectively. At this point intermediate E3 can

either undergo another C-C bond β -scission to form benzene and butadienyl, or through further cyclization it can form two fused six-membered rings (E4). The initial loss of H from C-1 forms 9,10-dihydronaphthalene. Naphthalene (P4) is then produced by H elimination from the two

fusing C atoms. From *cis*-9,10-dihydronaphthalene, two H atoms can also be eliminated simultaneously as H₂ and in this case the computed energy barrier is 75.53 kcal/mol. Pathway R6, on the other hand, forms benzene through the isomerization of fulvene. The initial C-C β -scission step from I1 to E1 is the same as in pathway R5. Instead of undergoing a three-membered ring closure as in pathway R5, E1 rearranges itself to form intermediate F1 through H atom shift. The following β -scission of the C-C bond produces fulvene (F2) and butadienyl radical. Fulvene forms isofulvene (F3) with a five-member ring and a three-member ring fused together. Cyclohexadiene carbene (F4) is formed with an energy barrier of 27.4 kcal/mol, and it then undergoes hydrogen migration to produce benzene.



The thermal isomerization of fulvene to benzene has been studied by Madden et al.⁴ with the modified Gaussian-2 (G2M) and BAC-MP4 methods. The authors investigated three mechanisms: a multi-step pathway for the thermal isomerization and two routes involving benzvalene as an intermediate, that are important for the photochemical benzene-fulvene isomerization. The pathway presented here is similar to the multi-step mechanism, except that we identified two transition structures in the reaction step from F3 to F4. One of the two structures corresponds to the transition state reported by Madden et al. (labeled as TS2 in Ref. 4) while the other is 4.4 kcal/mol lower in energy at the B3LYP/6-31G(d,p) level of theory.

In addition to pathway R6, fulvene can also be formed by combining CPDyl radical with the methyl radical produced in pathways R1 and R2, and then eliminating two hydrogen atoms. This reaction sequence is reported as route R7.

The potential energy surface diagrams for the reaction pathways R1-R6 are reported in the figure on the left. The values shown in the figures are inclusive of the zero-point energies $E = E_{\text{elec}} + \text{ZPE}$. The B3LYP method gives good estimations of the reaction energies, but it underpredicts the energetic barriers by 4-5 kcal/mol, and more accurate methods can be used in the future, such as BH&HLYP/6-31G(d,p).¹²

The BH&HLYP method predicts rather accurate barrier heights, particularly for hydrogen abstraction reactions by a radical in comparison with more expensive calculations.¹³

The computational results reported above are in qualitative agreement with the experimental observations reported in section 1.1.1: the PAH products from dicyclopentadiene (DCPD) pyrolysis at 550-850 °C, temperatures below which ring fragmentation pathways are dominant, were numerous. Some of the identified products are formed through reactions similar to the one reported in the radical-radical mechanism of Melius and coworkers⁴ for the conversion of two CPDyl radicals to naphthalene, but other observed products are instead more likely produced through different mechanisms.

The major products from CPD pyrolysis were benzene, indene and naphthalene. The formation of benzene and indene supports the existence of radical-molecule pathways¹⁻² in addition to radical-radical pathways producing naphthalene.⁴ Experimentally, the amount of indene produced exceeds that of naphthalene and benzene at low temperatures and then the concentration profile of indene starts to decrease at 750 °C where naphthalene represents the major product. The computed pathways R1 and R2 have the lowest energy barriers among the various reaction channels so it is reasonable to assume that indene will be the major compound produced at low temperatures. Between the intramolecular additions that lead to indene, pathway R1 is apparently more favorable since the energy barrier is 17.85 kcal/mol from I1 to A1, compared with the 32.06 kcal/mol required for the transition from I1 to B1. As the temperature increases, the C-H bond β -scission and the C-C bond β -scission pathways become significant. As a result naphthalene and benzene are produced.

An important result obtained in this study is the identification of additional energetically favored pathways for the formation of naphthalene and benzene via C-C bond β -scission. In fact, the barrier from I1 to E1 is lower than the one from I1 to C1 + H or D1 + H, being 41.21 kcal/mol for the C-C bond β -scission reactions because of relatively weak C-C bond compared with 48.45 and 45.13 kcal/mol for the cleavage of the C-H bond in pathways R3 and R4.

In addition to these major products, C₁₀H₁₀ compounds such as methyl indene, dihydrofulvalene, and dihydronaphthalene were also observed in the experiment. The existence of these compounds further confirms the intramolecular addition, C-H bond β -scission, and C-C bond β -scission pathways identified on the basis of quantum mechanical computations. Experimentally, an unidentified C₁₀H₁₀ compound was reported and its mass spectrum excluded the possibility of being dihydrofulvalene. As shown in pathway R5, intermediate E3 can either undergo a C-C bond β -scission to form benzene and butadienyl, or eliminate a hydrogen atom to produce phenyl-butadiene (C₁₀H₁₀) with the energy barrier being 26.65 kcal/mol for the latter. We suspect that the unknown C₁₀H₁₀ compound detected in the experiment might be phenyl-butadiene.

Other aromatic products experimentally observed include toluene, styrene, fluorene, phenanthrene, and anthracene, which can be formed through reactions with smaller aromatic products. As soon as benzene is formed it can undergo H abstraction to produce C₆H₅ radical¹⁴ that can react with the CH₃ radical produced from pathways R1 and R2 to form toluene.¹⁵⁻¹⁸ In the same way, once indene is formed it can react with the CPDyl radical to produce fluorene, phenanthrene, and anthracene.^{2,19}

All of the pathways described above share the same initial step that consists in the addition of cyclopentadienyl radical to π -bond of cyclopentadiene $\text{CPD} + \text{CPDyl} \rightarrow \text{I1}$. The second step differentiates the pathways analyzed. It is important to point out that all the pathways analyzed consist of a series of sequential reactions, and the rate determining steps need to be identified to

fully understand the kinetics. However, by comparing simply the branching step rates we can still get an idea of the relative importance of the alternative channels. At lower temperatures the intramolecular addition pathways R1 and R2 are dominant, which is in agreement with the experimental results that the yield of indene is larger than that of naphthalene and benzene at temperatures lower than 750 °C. As the temperature increases, the entropy contribution becomes significant, and the C-C bond β -scission and C-H bond β -scission rates increase quicker than the intramolecular addition rate. The temperature dependent pattern of rate constants suggests that the C-C bond and C-H bond β -scission pathways are entropically favorable.

The H elimination steps in the pathways proposed above are considered to occur through unimolecular β -scission reactions, but in a H-rich environment bimolecular H-abstraction reactions need to be considered too. For the systems studied in this paper, it is possible to identify two classes of H elimination reactions: a) the unpaired electron left on the carbon is delocalized to form a resonantly stabilized free radical and b) a conjugated double bond with other π electrons is formed, which significantly stabilizes the system.

For the class a), the first reaction calculated is $C_5H_6 + H = C_5H_5 + H_2$ with the energy barrier being only 1.18 kcal/mol, which is much lower than the energy required for H elimination being 78.6 kcal/mol. The low barrier is attributed to that the hydrogen to be removed was bonded to a saturated carbon atom, in comparison with the barrier being 10-20 kcal/mol¹² for the hydrogen abstraction from an unsaturated double-bonded carbon in PAH.

Similarly, reaction $C1 + H = D3 + H_2$ has a barrier of 0.18 and $G1 + H = G2 + H_2$ 0.16 kcal/mol. Transition state has been located for the reactions $D1 + H = D2 + H_2$ and $E5$ (*cis*-9,10-dihydronaphthalene) + $H = D7 + H_2$ with the energy 0.25 and 0.39 kcal/mol lower than the reactant after ZPE correction, indicating that loss of H from these species happens fast in a H-rich environment. Class b) includes the H abstraction from a saturated carbon of a resonantly stabilized radical to form more stable conjugated double-bond structure. Reactions $I1 + H = C1$ (or $D1$) + H_2 , $D7 + H = P4 + H_2$, $E4 + H = E5 + H_2$, $G2 + H = F2 + H_2$ follow in this category and no transition state has been identified for these reactions at the level of theory employed.

The potentially low energy barrier identified for the first class of H-abstraction reactions and other supporting evidences in the literature however give us great confidence that the reactions in both cases happen rapidly, for example, reaction $i-C_4H_3 + H = C_4H_2 + H_2$ ²⁰ has zero activation energy; no transition state was found for abstraction of H from phenyl and acenaphthylene adduct at the B3LYP/6-31G(d,p) level. As mentioned before, the B3LYP/6-31G(d,p) level of theory is inadequate for hydrogen abstraction reactions by radicals while BH&HLYP performs much better in this regard.¹²⁻¹³

Since the H elimination steps are mostly involved in the pathways leading to naphthalene, in a H-rich environment the formation rate of naphthalene will be greatly improved. The experiment shows that naphthalene yield is greater than indene above 1000 K while the rate constant calculation for the branching step shows that the crossover is at 2000 K. This discrepancy might be explained by including H-abstraction reactions. As emphasized earlier, a chemical kinetic model is needed for quantitative analysis of the reactor.

Another explanation for the discrepancy between experimental and computed kinetic results on the temperature at which the naphthalene yield becomes greater than the indene yield is that the radical-radical pathway of naphthalene formation is competitive with the radical-molecule pathway. The formation of benzene and indene supports the existence of the CPD-CPDyl addition pathway, while naphthalene can be formed by either the CPD-CPDyl addition or the CPDyl-CPDyl recombination pathway. The radical-radical reactions can occur at much higher

rates than the molecule-radical reactions. In addition, the bond formed in the initial adduct of these reactions is expected to be much stronger than that of the molecule-radical reactions, thus providing greater opportunity for rearrangement and cyclization. For instance, the initial CPD-CPDyl adduct I1 lies only 8.71 kcal/mol below the reactants, while the CPDyl-CPDyl adduct C1 lies 39.46 kcal/mol below the reactants. However in H-rich environment I1 can readily undergo H-abstraction to form C1 or D1. Besides, the energy barrier for I1 to decompose to CPD and CPDyl is 20.19 kcal/mol, which is likely to give I1 lifetime long enough for rearrangement as in the molecule-radical pathways proposed for the formation of indene and benzene.

The kinetic mechanisms identified for the pyrolysis of CPD include intramolecular addition and C-H bond β -scission for the production of indene and naphthalene. New mechanisms that involve the C-C bond β -scission reaction are identified for the production of benzene, fulvene, and naphthalene.

The formation of other aromatic compounds observed in the experiments such as toluene, styrene, fluorene, phenanthrene, and anthracene was also explained by subsequent reactions of smaller aromatic compounds, for instance benzene and indene. Rate constants for the first step of the pathways were calculated using the transition state theory, which show that at low temperatures the yield of indene is the largest among the three while at high temperatures benzene tends to dominate, in agreement with the experiments. In a H-rich environment, H-abstraction reactions by H-atoms are considered and they greatly improve the formation rate of naphthalene.

The computational results obtained in this project provide information for further investigation of the importance of the cyclopentadienyl moieties in the growth of PAH and additional studies that involve the use of a detailed kinetic mechanism for the formation of aromatics in a plug flow reactor have been already planned.

2.2 Cyclodehydrogenation reactions to Cyclopenta-fused PAH

B3LYP/6-31G(d,p) electronic structure calculations have been employed to elucidate the reaction mechanisms for the conversion of the alternant $C_{18}H_{12}$ PAH benzo[*c*]phenanthrene into the non-alternant $C_{18}H_{10}$ PAH cyclopenta[*cd*]pyrene and benzo[*ghi*]fluoranthene. Isomerization reactions such as 5/6-ring switching and hydrogen atom scrambling are analyzed. Bay region chemistry, involving the rupture of one benzene ring followed by the formation of new five-membered ring, is also studied, together with the mechanism for the formation of aryne. The rearrangement of the latter yields annelated cyclopentadienylidenecarbene, which is then trapped intramolecularly.

2.2.1 Reaction Pathways

Benzo[ghi]fluoranthene formation

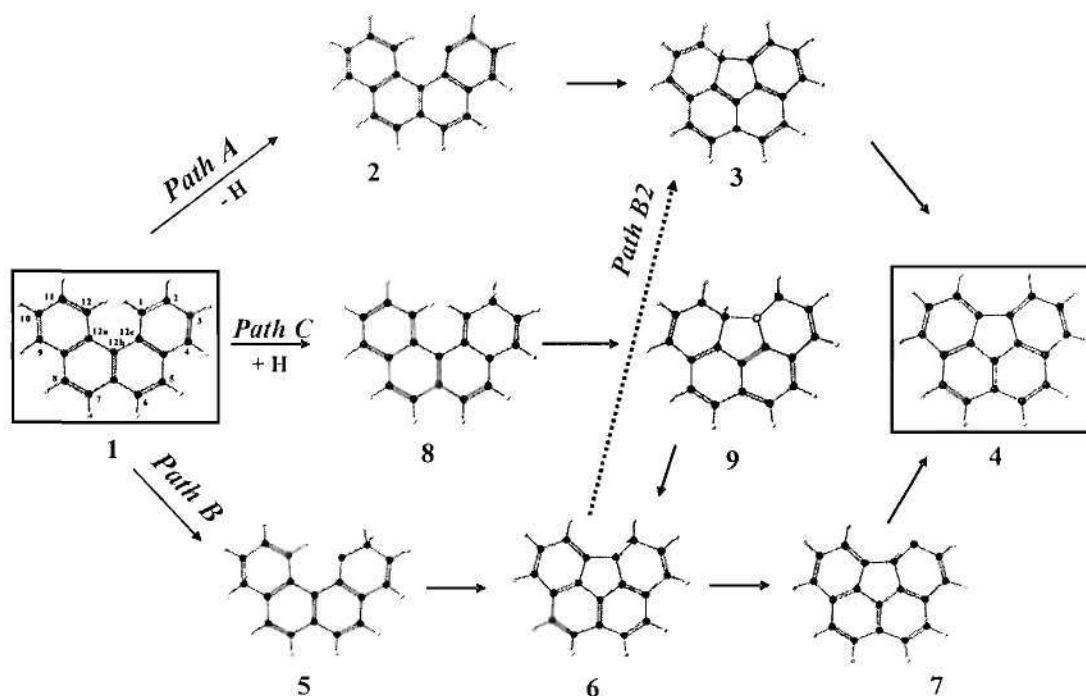
The figure below shows three possible pathways for the conversion of benzo[*c*]phenanthrene to benzo[*ghi*]fluoranthene.

Path A: The cyclodehydrogenation of benzo[*c*]phenanthrene (**1**) may proceed through the initial abstraction of hydrogen from C1 to produce radical **2**. The removal of hydrogen lessens the steric congestion present in the parent aryl: the interring dihedral angle in **2** is 0 degrees

whereas in **1** is 18 degrees. As already mentioned, since the energy of the homolytic C-H bond cleavage in PAH is governed by steric rather than electronic effects hydrogen abstraction from position 1 is favored over the others by about 7 kcal/mol.

Radical **2** is predicted to readily undergo intramolecular ring closure to intermediate **3**. The transition state of this reaction is found to be quite early, with the length of the C-C bond under formation amounting to ca. 2.17Å in the transition state. The partial loss of aromaticity that accompanies the ring closure offsets the energy gains due to formation of C-C bond, resulting in a predicted reaction energy of -7.6 kcal/mol.

C-H bond cleavage completes the pathway from **1** to benzo[ghi]fluoranthene (**4**), where the aromaticity is restored upon the removal of hydrogen. This process involves a transition state energy of 25.3 kcal/mol. The present calculation places the products **4** + H₂ 15 kcal/mol above the reactant. Thus, once formed, compound **2** is rapidly converted to pericondensed PAH and H in a two-step process with low energy barriers.



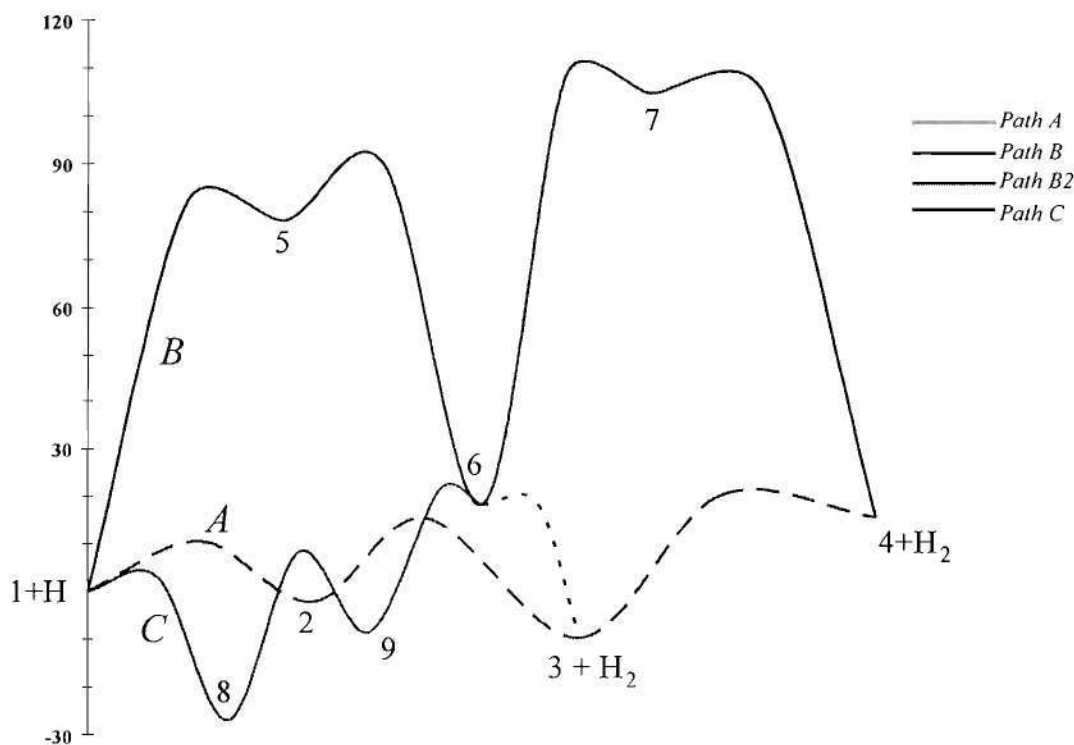
Path B: The formation of benzo[ghi]fluoranthene can also progress through a 1,2-shift of hydrogen out of the cove region to the adjacent carbon to produce radical **5**. The energy barrier for this reaction was identified to be 81 kcal/mol. This type of scrambling of hydrogen atoms represents an important thermal reaction for PAH.²¹ In **5**, the 1,5 hydrogen shift between the atoms C1 and C12 is facilitated by their proximity. As a consequence, a further H migration from C12 leads to compound **6**, that is placed 18 kcal/mol in energy above the reactant **1**. The predicted reaction barrier for this reaction is 11.8 kcal/mol. The elimination of the two hydrogens bonded to the sp³ C2 produces intermediate **7** and the further H migration from the C1 to C2 leads to benzo[ghi]fluoranthene. The reaction barriers involved in these last two steps are: 90.15 kcal/mol for the **6** → **7** transition and 0.2 kcal/mol for the **7** → **4** transition, respectively. This indicates that once **7** is formed, it is rapidly converted to benzo[ghi]fluoranthene. As an alternative, from intermediate **6** the reaction can proceed through H abstraction of one of the two

hydrogens bonded to C2 to produce radical **3** (dotted line). The barrier energy for this H abstraction is 18.4 kcal/mol. From intermediate **3** the reaction route is similar to *Path A* and benzo[ghi]fluoranthene is formed through C-H bond cleavage in intermediate **3**.

The 1,2-elimination of molecular hydrogen from compound **6** to produce directly compound **4** is forbidden by orbital symmetry.

Path C: The conversion of benzo[*c*]phenanthrene to benzo[ghi]fluoranthene can also be initiated by the addition of a hydrogen atom to the 2-position of benzo[*c*]phenanthrene producing intermediate **8**. Whereas abstraction is close thermoneutral when the abstracting reagent is a hydrogen atom, the addition of a hydrogen atom to benzo[*c*]phenanthrene is quite exothermic - 26.95 kcal/mol and the activation energy is 2.84 kcal/mol. The resulting radical can then undergo conrotatory ring-closure forming a trans-ring junction (compound **9**) that then loses a hydrogen atom to give intermediate **6**. This type of electrocyclic reactions involves the exchange of π -bonds for ring-closing σ -bonds. Ring closure occurs when both orbitals rotate in the same direction to achieve overlap. In other words, conrotatory ring closure occurs when the top lobe of one orbital has the same phase as the bottom lobe of the other orbital involved in forming the sigma bond. At this point, the reaction pathway can either progress in the same way as *Path B* forming first intermediate **7** and then benzo[ghi]fluoranthene through H migration, or as in *Path B2* producing first radical **3** and then benzo[ghi]fluoranthene.

The figure below shows the B3LYP/6-31G(d,p) energy profiles for *Pathways A, B, and C*.

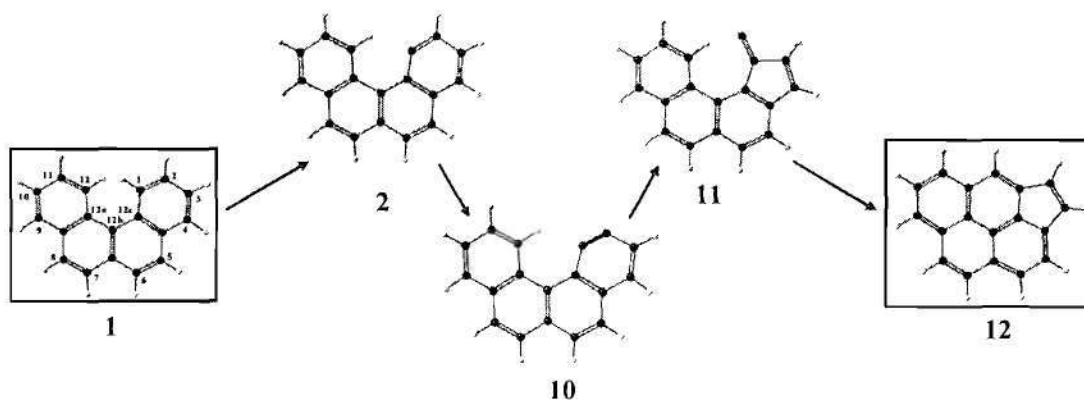


Pathways *A* and *C* are facilitated by the presence of radicals in the environment and they represent the principal sources for the production of benzo[*ghi*]fluoranthene in the presence of H atoms.

In a H-poor environment pathways *A* and *B* become competitive. The initial dehydrogenation step to produce compound **2** in pathway *A* requires the elimination of an H atom from **1** and the bond dissociation energy is found to be 103.2 kcal/mol. This result is similar to the one obtained by Cioslowski *et al.*³⁹ who identified the energy for the H loss from 1-phenylnaphthalene at BLYP/6-31G** level to be around 105 kcal/mol. As a consequence, in a H-poor environment the first steps involved in pathways *A* and *B* have both significant energy barriers (the transition energy for **1** → **5** is 81 kcal/mol), and they can both contribute to the formation of benzo[*ghi*]fluoranthene.

Cyclopenta[*cd*]pyrene formation

The figure below shows the reaction pathway *D* for the conversion of benzo[*c*]phenanthrene to cyclopenta[*cd*]pyrene.



Path D: The formation of cyclopenta[*cd*]pyrene from benzo[*c*]phenanthrene can be rationalized by invoking the benzyne-cyclopentadienylidene carbene rearrangement, i.e. the formation of 1,2-dehydrobenzo[*c*]phenanthrene via homolysis of a peri aryl C-H bond,²² followed by loss of a vicinal hydrogen. When exposed to radicals, for example in flame conditions, the aryl radical **2** may undergo further dehydrogenation forming compound **10**, where the H bonded to C2 has been removed. The energy barrier for the H abstraction from intermediate **2** by H atom is 13.6 kcal/mol at the B3LYP/6-31G(d,p) level of theory.

Benzyne benzologue **10** will produce its carbene isomer **11**, which then gives cyclopenta[*cd*]pyrene (**12**) via intramolecular trapping (C-H insertion).

The energy barrier for the reaction **10** → **11** is 41.3 kcal/mol. Only the singlet electronic state was considered for compound **11** (singlet -691.82 Hartree, triplet -691.76 Hartree, quintet -691.69 Hartree) in agreement with recent electronic structure calculations on cyclopentadienylidenecarbene.²³ The reaction energy for **10** → **11** is almost the same as that of the benzyne cyclopentadienylidenecarbene rearrangement (24.28 kcal/mol vs 29.28 kcal/mol), also in agreement with the results reported by Cioslowski *et al.*³⁹ The computed lengths of the analogous C-C bonds in **11** and cyclopentadienylidenecarbene are quite similar, indicating the

lack of significant conjugation between cyclopentadiene and six rings moieties. The highly exothermic cyclization which involves formation of a C-C bond concurrent with a 1,2-hydrogen shift, is predicted to possess activation enthalpy of only 7.6 kcal/mol. The products, cyclopenta[cd]pyrene + 2H₂, lie 94 kcal/mol below the reactants (1+2H).

In a H-poor environment, the benzine pathway to form intermediate **10** requires significant energy since the dissociation bond energy to form **10** from radical **2** is computed to be 86.2 kcal/mol.

From benzo[ghi]fluoranthene to cyclopenta[cd]pyrene

The conversion of benzo[ghi]fluoranthene to cyclopenta[cd]pyrene is an example of the Stone-Wales rearrangement, which involves the transposition of two sp²-hybridized carbon atoms within a framework of other sp²-hybridized atoms. Mechanisms for the Stone-Wales rearrangement have been extensively discussed,²⁴⁻²⁵ and it has also recently been pointed out that radical-promoted mechanisms can be energetically very favorable.²⁶ Below we report reaction pathways involving unimolecular and bimolecular reactions for the interconversion of benzo[ghi]fluoranthene into cyclopenta[cd]pyrene.

Unimolecular reactions

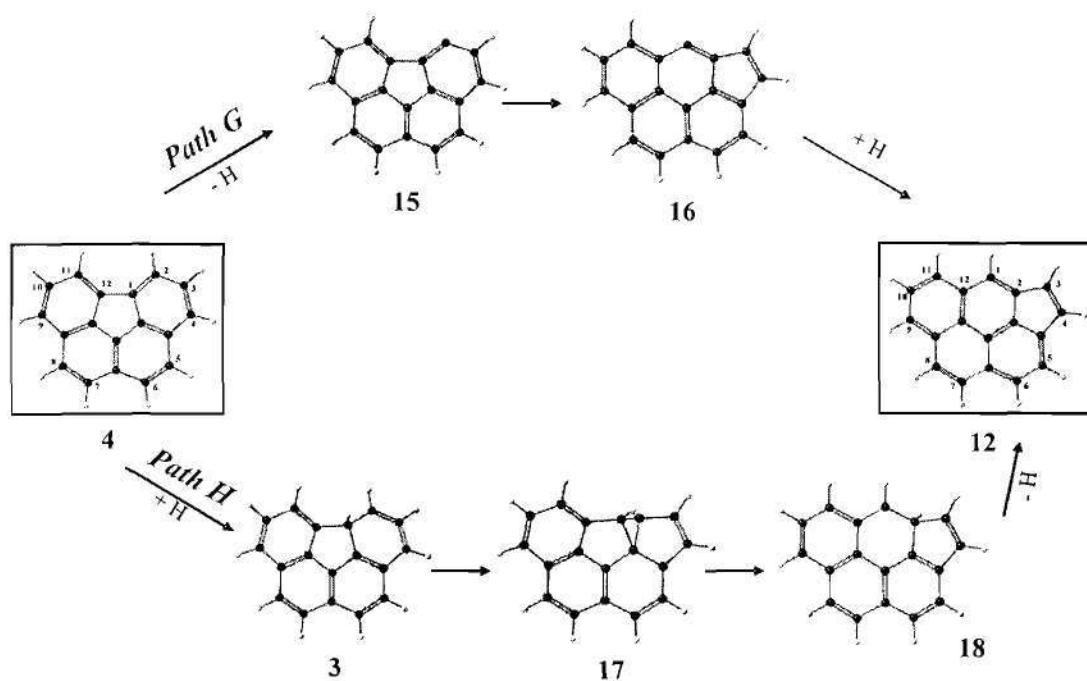
Since the original work of Scott and Roelofs¹⁰ on the 5/6-ring interconversion, many examples have been found^{29-30,35,38,27-28} and the process appears to be common among CP-PAH at high temperatures in the gas-phase. The ring-contraction/ring-expansion sequence, i.e. the exchange of a five- and six-membered ring can be achieved breaking one C-H and one C-C bond while forming one C-H and one C-C bond¹⁰ (*Pathway E*). In a similar way, a four-centered reaction involving concurrent breaking of two C-C bonds (C2-C3 and C12-C1) and forming of two C-C bonds can be considered for the production of cyclopenta[cd]pyrene from benzo[ghi]fluoranthene (*Pathway F*). The energy barriers for pathways *E* and *F* are 161.6 and 163.3 kcal/mol, respectively.

Bimolecular reactions

In the presence of H atoms, benzo[ghi]fluoranthene can undergo H abstraction to produce intermediate **15** and H₂ as shown in the figure below (*Pathway G*).

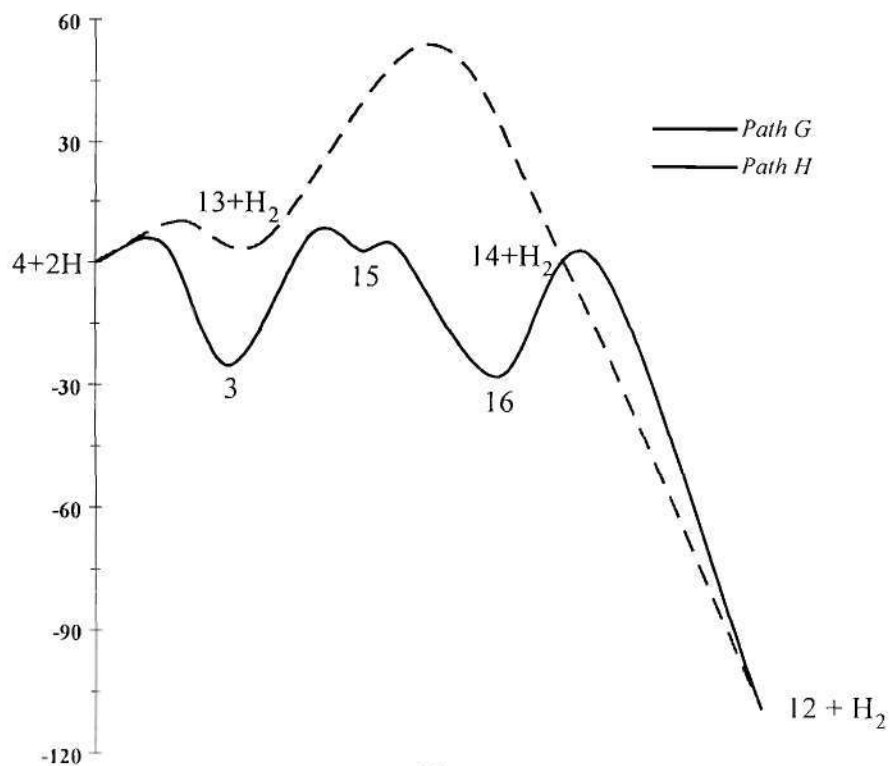
The energy barrier and reaction energy for the reaction **4** → **13** are 9.9 and 4.8 kcal/mol, respectively. The following ring opening/ring expansion reaction leading to intermediate **14** has an energy barrier of 49.0 kcal/mol. H atoms from the gas phase can then add to the radical on **14** to produce cyclopenta[cd]pyrene. The reaction energy for **14** + H → **12** with the zero-point energy correction is -110 kcal/mol.

Pathway H in the figure above represents another possibility for the interconversion of benzo[ghi]fluoranthene to cyclopenta[cd]pyrene by a radical-promoted route. H atom addition to compound **4** produces radical (**3**) – same as in *Pathway A* – that can then undergo ring closure to a cyclopropane (**15**), initiating the rearrangement. The energy barrier for the reaction **3** → **15** is 32.3 kcal/mol.



The 5/6 ring interconversion proceeds then through the formation of intermediate **16** where the C1-C12c bond is broken and the 6-membered ring is formed. The barrier for the reaction **15** → **16** reaction is 1.15 kcal/mol. Further H removal from C2 leads to cyclopenta[*cd*]pyrene.

The figure below shows the B3LYP/6-31G(d,p) energy profiles for *Pathways G* and *H*.



The present study identifies possible reaction pathways connecting benzo[*c*]phenanthrene to benzo[*ghi*]fluoranthene and cyclopenta[*cd*]pyrene, respectively. For the conversion of benzo[*c*]phenanthrene to benzo[*ghi*]fluoranthene, the first route involves H elimination to form radical **2**, followed by rapid cyclization to intermediate **3** and further H elimination to yield benzo[*ghi*]fluoranthene. The second pathway consists of scrambling of hydrogen atoms: first the 1,2-shift of hydrogen to produce compound **5** followed by 1,5-hydrogen shift to produce benzo[*ghi*]fluoranthene. The third route is represented by an electrocyclic reaction which is a type of pericyclic chemical reaction where the net result is one π bond being converted into one σ bond. The reaction proceeds by way of a cyclic transition state and one sigma bond is formed (intermediate **9**) during the course of the reaction (*Pathway C*).

Cyclopenta[*cd*]pyrene is formed through dehydrogenation of intermediate **2** to form the corresponding benzyne benzologue. The transient carbene is trapped via an intramolecular C-H insertion giving the cyclopenta-fused product.

For the conversion of benzo[*ghi*]fluoranthene to cyclopenta[*cd*]pyrene, four different mechanisms have been identified. The first two rearrangement pathways involve the formation of four-centered reactions: the direct ring-contraction/ring-expansion mechanisms show significant energy barriers (around 160 kcal/mol, in both cases). The other two routes are promoted by H atoms and cyclopenta[*cd*]pyrene is formed through 5/6 ring interconversion. Reaction rates and thermodynamic properties have been computed for all the species involved in the pathways.

These results provide an important context for the study of much larger PAH, fullerenes, nanoparticles, and soot. During combustion processes, the formation of high molecular mass structures, such as nanoparticles, and their conversion to mature soot aggregates is the result of a carbonization process involving formation of activated complexes, molecular rearrangement, polymerization, and dehydrogenation.²⁹⁻³⁰ Cyclodehydrogenation reactions are responsible for the surface rearrangements of carbonaceous particles and their reactivity and they need to be included in model descriptions for soot growth.

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Collaborative Research: Polycyclic Aromatic Hydrocarbon Growth Mechanisms in Combustion involving Cyclopentadiene and Indene

Project Participants

Senior Personnel

Name: Mulholland, James**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Zhu, Guangxuan**Worked for more than 160 Hours:** No**Contribution to Project:**

Dr. Zhu of Georgia Tech has provided assistance in the sampling of higher molecular weight polycyclic aromatic hydrocarbons.

Post-doc

Name: Ryu, Jae**Worked for more than 160 Hours:** No**Contribution to Project:**

Dr. Ryu of Georgia Tech has provided assistance in the sampling and analysis of polychlorinated naphthalenes and dioxins.

Graduate Student

Name: Kim, Do**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Do-Hyong Kim of Georgia Tech is conducting doctoral research on experimental studies of carbon growth in flames by reaction of cyclopentadienyl moieties.

Name: Wang, Huabing**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Huabing Wang of the University of Utah is conducting doctoral research on computational studies of carbon growth in flames by reaction of cyclopentadienyl moieties.

Name: Michalski, Grant**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Grant is earning an MS in environmental engineering at Georgia Tech and conducted experiments to investigate effects of residence time on the combustion chemistry of interest.

Undergraduate Student

Technician, Programmer

Other Participant

Name: Violi, Angela**Worked for more than 160 Hours:** Yes

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Project Participants

Senior Personnel

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Dr. Zhu of Georgia Tech has provided assistance in the sampling of higher molecular weight polycyclic aromatic hydrocarbons.

Post-doc

Name: Ryu, Jae**Worked for more than 160 Hours:** No**Contribution to Project:**

Dr. Ryu of Georgia Tech has provided assistance in the sampling and analysis of polychlorinated naphthalenes and dioxins.

Graduate Student

Name: Kim, Do**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Do-Hyong Kim of Georgia Tech is conducting doctoral research on experimental studies of carbon growth in flames by reaction of cyclopentadienyl moieties.

Name: Wang, Huabing**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Huabing Wang of the University of Utah is conducting doctoral research on computational studies of carbon growth in flames by reaction of cyclopentadienyl moieties.

Name: Michalski, Grant**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Grant is earning an MS in environmental engineering at Georgia Tech and conducted experiments to investigate effects of residence time on the combustion chemistry of interest.

Undergraduate Student

Technician, Programmer

Other Participant

Name: Violi, Angela**Worked for more than 160 Hours:** Yes